

Corrosion Resistance of Ni Electrodeposited Co Doped ZnO Nanocomposite Thin Films in NaCl Solution

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ABSTRACT: This work focuses on the atmosphere protected, ecological process by the combination of Cobalt doped Zinc oxide nanocomposites utilizing the extraction of Ocimum sanctum. The prepared nanocomposites are examined by unusual methods like Fourier transform infrared spectroscopy (FT-IR), X-ray Diffraction (XRD), Field emission scanning electron microscopy (FE-SEM), Energy Dispersive X-Ray Analysis (EDAX). A efficient study has been made on the result of Co doped ZnO nanocomposite for the anticorrosion behaviour of mild steel. The Co-ZnO nanocomposites of average diameter in the range 36 nm were coated on mild steel in nickel bath solution. The anticorrosion properties on the coated mild steel was carefully tested in 3.5% NaCl solution by performing potentiodynamic polarization measurement and electrochemical impedance spectroscopy. Surface morphology of the coated mild steel immersed in corrosive solution was judged by using SEM with EDAX. The Co-ZnO nanocomposites coating has shown a perfect protection against corrosion and the shielding capability is in the range of 95%. The incorporation of Co-ZnO nanocomposites has upgraded the process of mild steel in all corrosion media are subjected to the investigation.

KEYWORDS: Nanocomposite, SEM, EDAX, Electro deposition, electrochemical methods, electrochemical impedance, Mild steel

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INTRODUCTION

Zinc oxide is a semiconductor objects with a wide range of application including biosensors, catalyst and photovoltaic devices [1-5]. Various methods have been used to synthesize ZnO nanoparticles such as Sol-gel, radio-frequency (RF) sputtering, Chemical vapour deposition, pulsed laser deposition, and spray pyrolysis [6-10]. In addition, Zinc oxide lattices have been shown to contain various types of blemish helping them to behave as n-type semi-conductors due to zinc and oxygen vacancies and interstitial, as well as more complex defects [11-16]. Some research groups have modified ZnO properties through adding dopant materials such as N, Al, Ga, Cu, Mg and In, which can significantly enhance the electrical, dielectric and optical properties of ZnO [17,18]. CuO is a P-type semiconductor material used in a broad range of application including anti-corrosion properties, solar cells, bio sensors, gas sensor, super conductor, lithium-ion electrode materials, magnetic storage media, and field effect transistors [19-22] and its composite materials have recently attracted attention due to promising features in electrochemical behaviour [23, 24].

Corrosion is a common problem which significantly affects the properties of materials [25,26] and high resistance to corrosion is

attributed to the spontaneous development of a chemically stable oxide film surface [27-29]. Transition metal oxide and conducting polymers are the promising candidates due to their strong bonding structure which can be withstanding in diverse applications including anticorrosion applications [30-33]. From the detailed investigation of earlier literatures, we have prepared Co doped ZnO nanocomposite thin film by eco- friendly method. To the best of our knowledge, there are no reports available on the extract synthesis of Co doped ZnO nanocomposite. The structural, compositional, morphological and electro chemical properties of the prepared nanocomposite film were studied in detail.

MATERIALS AND METHODS

Chemicals

Ocimum sanctum leaves were collected from local agriculture fields, Salem. Tamilnadu. India. Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$) and Cobalt acetate ($\text{Co}(\text{CH}_3\text{COO})_2$) and citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) was purchased from Ranbaxy fine Chemicals and Na_2CO_3 from ADLAB Chemicals.

Synthesis of Cobalt doped ZnO Nanoparticle using Ocimum Sanctum Leaf Extract

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Ocimum sanctum leaves was collected and washed in distilled water, impurities are removed like scum, dust from the deionized water. After drying the same at 30 °C a sample of 15 g was taken for nanomaterials synthesis and boiled with 150ml of de-ionized water for 15 min at 80 °C. As a result, a light greenish yellow colored solution was found and then it is cooled at room temperature followed by decanting the greenish yellow colour extraction. A solution of Zinc acetate and Cobalt acetate with citric acid was prepared in de-ionized water under constant stirring and then added in plant extract drop by drop. The above solution was continuously stirred for about 2 h by using magnetic stirrer. The next step is adding up of sodium carbonate solution, a grey color precipitate was formed at pH 6. The collected precipitate washed and dried for about 10 days. At the end of the 10th day, grey color precipitate was obtained. The precipitate was powdered using pestle and heated at 600°C for 2 h. The resultant pure grey powdered product of Cobalt doped ZnO Nps was obtained.

Preparation of Specimen

The mild steel coupons of dimension 1 x cm² was cut and used for corrosion studies. The emery paper was used to polish the surface of the steel coupons so that the existing passive film was removed.

Electro deposition Process

Electro deposition process was performed in a nickel plating bath. As mentioned in Table 1, the analytical grade of NiSO₄, NiCl₂, H₃BO₃ was used to prepare the nickel bath electrolyte.

Table 1. Nickel bath electrolyte

Composition	Concentration
NiSO ₄	246 g/L
NiCl ₂	20 g/L
H ₃ BO ₃	40 g/L
Co-ZnO	0.1 0.5 g
pH	4-5
Temperature	RT
Stirring rate	350 rpm
Time	30-40 min
Current density	2.5 mA/cm ²

The application of electrode position produced a better result of adhesion of coating. Further the throw power was also improved to a great extent including an enhanced cross linking efficiency. The high performance coating capacity clubbed with an excellent corrosion resistance attract the industries to make use of this type of electro

deposition. The anode (Ni) and cathode (base material) test cell set up was placed on the magnetic stirring hot plate. The electrolyte pH value is maintained at 4.5-5.0 to examine the electrodeposition process. The distinct deposition time ranging between (30 and 40 min) and current density of 2.5 mA/cm² was applied. Rinsing the sample with mineral water and drying the same at ambient temperature formed the final task.

Characterization Methods

The X-ray diffraction (GE Inspection Technologies, Model No.3003 TT, Make: Germany Operation Voltage: 40 kV Current: 40 mA) was used to study the crystal structure of the Cu- ZnO Nps. Functional group of the mixture observed by utilizing Fourier Transform infrared spectroscopy (Perking Elmer Model: Spectrum RXI Range:4000 nm -400 nm). Morphology, topography and the particle size were differentiated by making use of field emission scanning electron microscope (FESEM). The sample composition was studied by means of energy dispersive X-ray analysis (EDX) (Make: JEOL, Model:JSM 6390, Japan).

UV-Visible Spectral Analysis

The UV-Vis absorbance spectrum of Cobalt doped ZnO Nps is shown in Figure 1. Cobalt doped ZnO Nps shows a blue shifted absorption of maximum 374 nm. The shift in absorption clearly shows that the addition of Cobalt is in ZnO lattice. The energy band gap of Cobalt doped ZnO was estimated as 3.3 eV (34). The optical band-gap of the Co-ZnO nanoparticles can be determined with a well-known Tauc's model by using Mott and Davis relation $\alpha h\nu \sim (h\nu - E_g)^{1/2}$. Where E_g is energy band gap the band gap is obtained by extrapolating the tangential line of $(\alpha h\nu)^2$ to the photon energy axis. From Figure 1, the band gap energy for Co doped ZnO nanoparticles are found to be 3.05 eV range and for pure samples 3.28 eV.

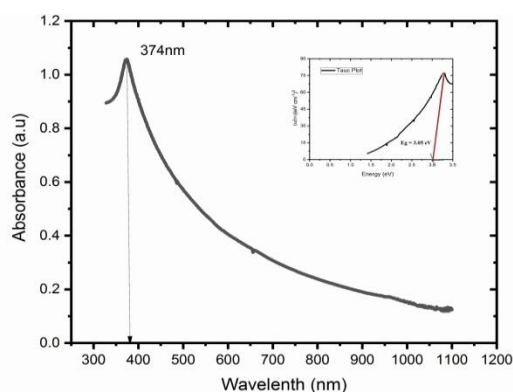


Figure 1 UV-Vis absorption spectra of Cobalt doped ZnO Nps

The doping of cobalt with ZnO nanoparticles leads to the reduction in band gap energy 3.05 eV. This is due to the increase in particle size that results in the less quantum confinement within the nanoparticles which is consistent with our FT-IR results [35]. Also the reason for reduction in band gap is mainly due to the sp-d exchange interaction between the localized d electrons and p electrons [36]. The reduction in band gap may be attributed to the increase in charge carrier concentration in Co doped ZnO nanoparticles [37].

FT-IR Spectral analysis

The FT-IR spectrum of the prepared Co doped ZnO is shown in Figure 2. The peak observed at 510 cm^{-1} in Co doped ZnO confirmed the presence of stretching mode of ZnO [38]. The broad absorption band at 3226 cm^{-1} is attributed to O-H stretching, which is assigned to chemisorbed and/or physisorbed H_2O molecules on the ZnO surface. Another absorption band at 1650 cm^{-1} is attributed to H-O-H bending vibration which is assigned to a small amount of H_2O in the ZnO nanoparticles [39]. The C=O stretching band was observed at 1543 cm^{-1} . The C=O band was observed at 1415 cm^{-1} . The band at 850 cm^{-1} indicates the presence of Zn-Co-O micro structural changes.

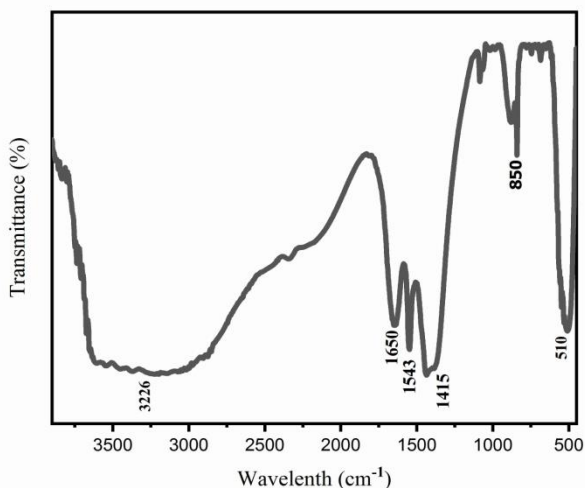


Figure 2 FT-IR spectrum of Cobalt doped ZnO Nps

Photoluminescence Analysis

In order to study the optical quality and presence of possible induced by dopant on the radiative emission process of Cobalt doped ZnO Nps. The peaks observed at 431 nm correspond to the blue emission [40]. The blue emission may be due to the self rapt excitons (STE) originated by interactions of conduction band electrons localized Zn d-orbital with holes present in the O

p-orbital. The Figure 3 shows the highest intensity peak present in the IR region at 751 nm which is related to the surface defect in pure ZnO is shielded after Cobalt doping. It is likely that the Co^{2+} in the ZnO lattice absorbs the energy from the defect emission, because the defect state energy is very close to the photon energy, which excites the transition of Co^{2+} ions providing competitive pathway for recombination and result in the IR region [41].

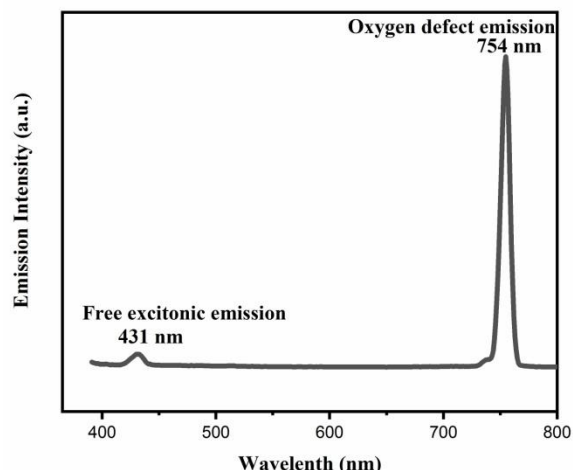


Figure 3 PL spectrum of Cobalt doped ZnO Nps

Particle size Analysis

Particle size analyzer is used to determine the size of individual particles as well as a size distribution range for a given sample. The average particle size of 15 nm was obtained for Cobalt doped ZnO Nps from the particle size distribution graph Figure 4

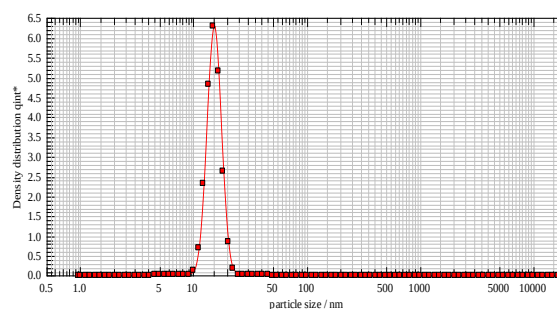


Figure 4 Particle size Analysis of Cobalt doped ZnO Nps

XRD Analysis

The XRD diffraction pattern taken on Co-doped ZnO nanoparticles clearly shows the hexagonal wurtzite ZnO structures in Figure 5. The phase purity and lattice parameters have been studied using powder X-ray diffraction and Scherrer equation. All the noticeable peaks at 2θ values 31.56, 34.22, 36.04, 47.29, 56.43, 62.71, 67.78, 68.90 with plane of reflection values 100, 002, 101, 102, 110, 103, 002 and 112 respectively [42].

visible light spectrum more active for the better photocatalytic activity [45].

Figure 1 consists of two SEM images. Image (a) shows a dense network of nanowires with a 1 μm scale bar. Image (b) shows nanowires with spherical Ag nanoparticles attached, with a 2 μm scale bar. Both images include labels for nanowire diameters and lengths.

EDAX Analysis

Cobalt Doped ZnO

Intensity (a.u.)

2 Theta

Peaks labeled: (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (002).

The EDS spectrum shows intensity versus energy in KeV. The x-axis ranges from 0 to 10 KeV, and the y-axis ranges from 0 to 14. Peaks are labeled for O (blue), Cs (green), Zn (magenta), and Cu (red). The O peak is at approximately 0.5 KeV, the Cs peak is at approximately 0.6 KeV, the Zn peak is at approximately 0.8 KeV, and the Cu peak is at approximately 8.9 KeV. There is also a small peak at approximately 2.1 KeV.

FE-SEM Analysis

RESULTS AND DISCUSSION

Potentiodynamic Polarization Measurements

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NaCl electrolyte found to be -0.994 V and the values for Co-ZnO Nps coated mild steel was ± 85 mV indicating the mixed type inhibitor. Corrosion current (I_{corr}) values decrease with increasing concentration of nanocoating on mildsteel. This represented that coating of Co-ZnO Nps inhibits the corrosion rate. The following equation calculates the rate of corrosion:

$$\text{CR (mils/y)} = (3.27 \times 10^{-3}) I_{\text{corr}} (\text{Eq.wt.}) / dx 0.0254 \quad (4)$$

Where, the Eq.wt refers to the equivalent weight of mild steel (28.25) and d is the density of the mild steel (7.85 g/cm³). The corrosion rate of mild steel in 3.5% NaCl electrolyte was found to be 48.21 mpy. The rust speed of Co-ZnO Nps covered mild steel was less than the uncovered metals.

The efficiency of inhibition computed using the formula

$$\text{IE\%} = (I'_{\text{corr}} - I_{\text{corr}}) / I'_{\text{corr}} \times 100 \quad (5)$$

Where I'_{corr} and I_{corr} are the present rusting values of metal in presence and in absence of Cu-ZnO Nps coating. The inhibition efficiency maximum at 95.74% for 3.5% NaCl with 0.5g Co-ZnO Nps was achieved. It was observed that the increase of the efficiency in the inhibition that corresponded with the raise of nanocoating concentration. Similarly the inhibition efficiency reduced along the raise in the denseness of aggressive medium. This could be because of the diffusion of corrosive chloride ions through the nanocoating. The next observation is that the inhibition efficiency also minimised with the higher concentration of Co-ZnO Nps above 0.5g. The weak adhesion of Nps resulted mainly because of collection at high concentration leading to weak deposition.

Table II. Polarization parameters of mild steel coated Co-ZnO Nps in NaCl

Conc. of NaCl %	Amount of Co-ZnO Nps in gms.	E _{corr} (V/SCE)	ba (mV dec ⁻¹)	bc (mV dec ⁻¹)	Corrosion I_{corr} (mA/cm ²)	Inhibition efficiency (%)
3.5%	Blank	-0.994	125.14	299.85	110.87	--
	0.1	-0.958	179.43	273.97	51.09	53.91
	0.2	-0.914	204.70	214.04	39.41	64.45
	0.3	-0.937	187.89	182.01	21.33	80.76
	0.4	-0.963	189.39	196.92	11.44	89.68
	0.5	-0.971	174.17	231.16	4.72	95.74

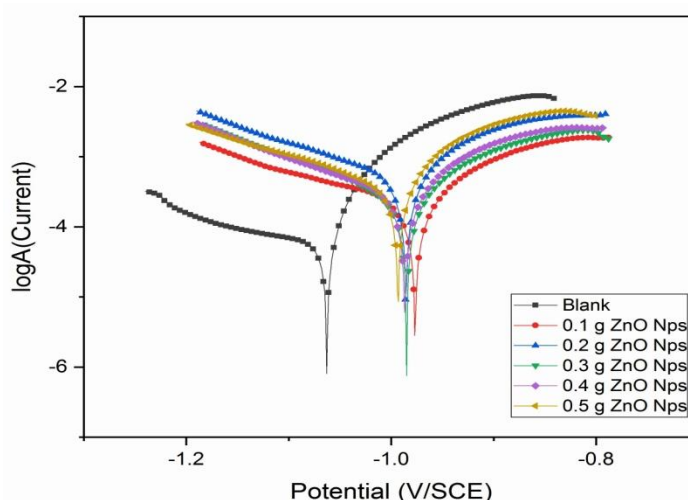


Fig. 8. Potentiodynamic curves for mild steel with various concentrations of Co- ZnO Nps in 3.5% NaCl.

Impedance Measurements

Fig.9 show the impedance measurements (EIS) carried out at 5 mV with a frequency range of 100 kHz to 10 mHz. The Nyquist plots offered the EIS values for suitable equivalent circuit that

comprises of solution resistance identified as (R_s) followed by coating capacitance noted as (Q_{coat}), next is coating resistance marked as (R_{coat}), succeeded by double layer capacitance recognized as (Q_{dl}) and finally the charge transfer resistance which is understood as (R_{ct}). Zsimpwin

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3.21software was used for this purpose and presented in Table III. The Constant Phase Element (CPE), a sign of the non-ideal homogeneity of the surface, replaced the capacitor.

$$Z_{CPE} = Y_0^{-1} (i\omega)^{-n} \quad (6)$$

In the above equation Y_0 represents the CPE which is a constant, $i^2 = -1$ is an imaginary number, ω is the angular frequency and n indicates the CPE component that gives the particulars related to the degree of homogeneity on the metal surface, micro-roughness and probity. The corrosion inhibition efficiency can be computed from the following equation

$$IE\% = R_p - R'_p / R_p \times 100 \quad (7)$$

Where R'_p and R_p represent the polarization resistance values of metal free coating with Co-ZnO Nps coating respectively. The Q_{dl} values steadily decreased for mild steel after the inclusion of Co-ZnO Nps from 0.1g to 0.5g. It was observed that 0.5g of Co-ZnO Nps layer on metal (mild steel) was optimum in 3.5% NaCl electrolyte. The minimum of Q_{dl} value was

observed for 0.5g in 3.5% NaCl. Similarly, higher R_{ct} value for mild steel and Co-ZnO Nps coating showed excellent corrosion resistance property without outside layer. The decrease in Q_{dl} and increase in R_{ct} value for Mild steel coated with Co-ZnO Nps denotes an increased obstruction among the interface of electrolyte and Mild steel. The coated metal surface made a greater stability and a meager amount of pores on its exterior area, resulting in a reduction of corrosion reactions on the surface of electrode. The mild steel with 0.5g Co-ZnO Nps coating registered a high impedance value. The output showed the highest inhibition efficiency of 96.41% in 3.5% NaCl electrolyte respectively. The higher the Nps thickness, the lower is the impedance value. This is due to the assemblage of Nps on mild steel during its coating which results in poor adhesion and porous deposits; as a result there was a decrease in impedance. Furthermore, decrement in impedance at higher concentration of NaCl electrolyte is due to the diffusion of chloride ions through nanocoating. The diffusion of chloride ions was proportional to its solution pressure which weakens the adhesion. The EIS outcome disclosed a superior corrosion resistance property of mild steel Co-ZnO Nps coating.

Table III. Electrochemical impedance data of Co-ZnO Nps coated mild steel in NaCl.

Conc. of NaCl %	Co-ZnO Nps in gms.	C_{coat} ($\mu F/cm^2$)	C_{dl} ($\mu F/cm^2$)	R_{ct} ($\Omega.cm^2$)	Inhibition efficiency(%)
3.5	Blank	1964.12	1903.49	36.83	--
	0.1	1123.58	1028.39	296.98	87.59
	0.2	973.60	829.64	368.82	90.01
	0.3	765.63	648.29	417.93	91.18
	0.4	431.01	381.50	990.21	96.28
	0.5	118.19	215.15	1028.00	96.41

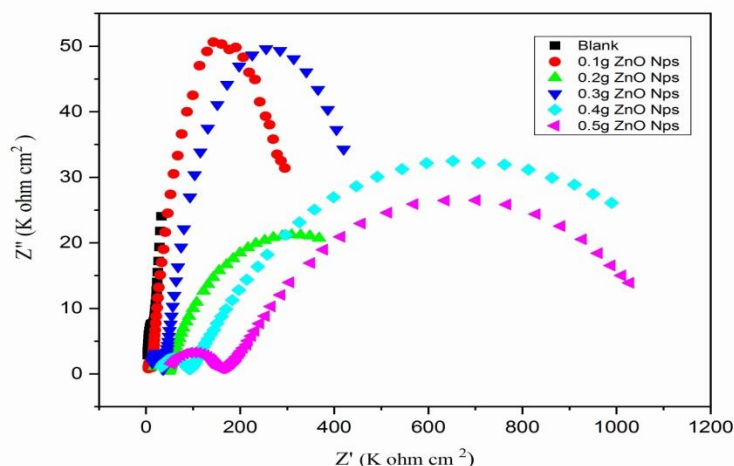


Fig. 9 (a) Electrochemical impedance curves for Co- ZnO Nps coated mild steel in 3.5% NaCl concentration

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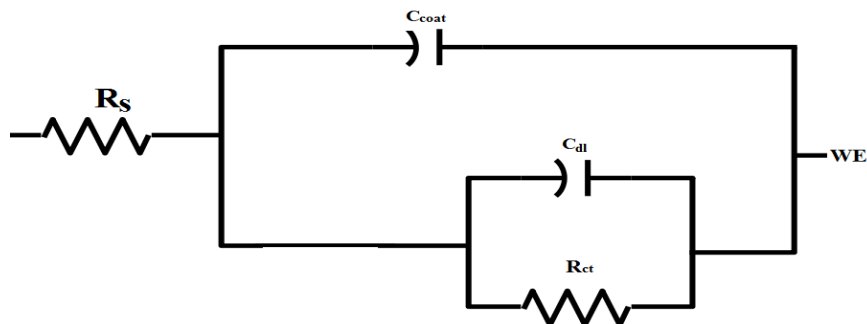


Fig. 9 (b) equivalent circuit describes the schematic of electrochemical reaction.

R_s - Solution resistance of 3.5%, WE - working electrode, C_{dl} - double layer capacitance, C_{coat} - coating capacitance, R_{ct} - charge transfer resistance, R_{coat} - coating resistance

Morphology Studies

Fig.10 (a) shows plain area of the metal (mild steel) and an emery paper used for polishing the surface in the mild steel to remove the existing film. Figure 10 (c) shows the plain metal dipped in 3.5% NaCl electrolyte kept for 24 h and the formation of rust on the surface of mild steel. This was caused by the diffusion of Cl^- to the mild steel exterior area that showed more dissolution of steel in NaCl medium. Furthermore, It was observed that the exterior area of mild steel had more corrosion patches and porous.

Co-ZnO Nps coated mild steel without immersion is shown in (Fig. 10(b)). The Co-ZnO Nps coated on the steel after immersion for 24 h in 3.5% NaCl electrolyte given in (Fig. 10 (d)), did not show any cracks or defects. The coating appeared more dense and uniform, homogeneous and continuous closed packed structure on mild steel and brought higher corrosion protection to the metallic substrate. It is known that Fe_2O_3 are rust composition and Co-ZnO forms as a passivation layer on the mild steel. It was examined that Co-ZnO nano coating on metals such as iron gave anodic protection and acted as electronic, chemical and physical obstacle to reduce anodic reaction and maintain high opposition to ionic flow. The obstructing the metal dissolution, provide a first-rate rust protection and it prevents electron transfer in 3.5% NaCl solution to achieve great corrosion inhibition.

The elemental composition of Co-ZnO nanomaterials was observed by EDX as shown in Fig.7 for the Co-ZnO coated samples, the percentage of Ni was 4.68%. In the doped samples for the Co are observed at 0.71%. In the pure ZnO the chemical composition is 82.56% respectively. The EDAX result shows the presence of Zn, O and Ni. The prepared nanoparticles are made of these elements. This may be Co^{2+} ions incorporated with Zn^{2+} ion in the ZnO matrix.

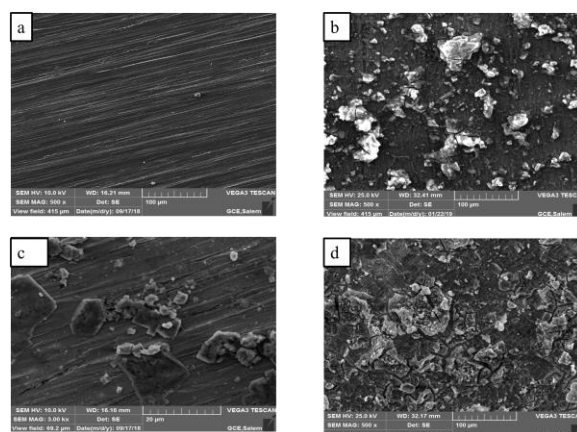


Fig. 10 SEM images of (a) bare mild steel (b) Co-ZnO Nps coated mild steel (c) bare mild steel immersed in 3.5% NaCl solution (d) Co-ZnO Nps coated mild steel immersed in 3.5% NaCl.

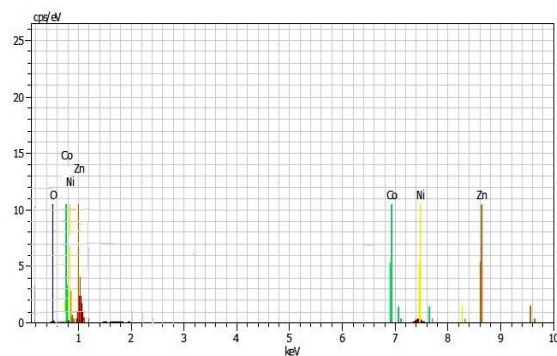


Fig. 11 EDAX pattern of Cobalt doped ZnO Nps coated mild steel immersed in 3.5% NaCl electrolyte

CONCLUSION

The corrosion resistance ability of Co-ZnO nanoparticle coated mild steel has been systematically studied. It has been inferred that the Co-ZnO Nps minimizes alloy reaction within zinc and iron consequent in the formation of inside layer of the mild steel surface leading to

irregular and porous surface. Co-ZnO Nps nanocoating layer enhances the adhesion between mild steel and coating layer and inhibits the dispersion of zinc. The Tafel polarization shows that the compound has a mixed type of inhibition. The excellent functioning of the inhibitor has been confirmed from Nyquist plots, where the improved adsorption of the Co-ZnO Nps nanocoating gradually retards C_{dl} at the expense of R_{ct} . A maximum inhibition efficiency was observed at 3.5% NaCl solution with 0.5g of Co-ZnO Nps by both polarization and impedance studies. The SEM and EDAX results showed better inhibition efficiency at 3.5% NaCl solution. The impedance studies revealed a maximum inhibition efficiency of 96% at 3.5% NaCl solution and 0.5g of Cu-ZnO Nps; whereas, the polarization studies confirmed the maximum inhibition efficiency of 95 %. Owing to the good performance at corrosive environments, Co-ZnO Nps coating proved to be highly suitable for industrial applications.

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